Microscopic observations of bitumen spreading at gas bubble surfaces

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ABSTRACT

Bitumen spreading at gas bubble surfaces was observed through a stereoscopic microscope for Whiterocks oil sand samples submerged in alkaline solutions. This phenomenon was also observed for model systems where air bubbles were placed al *the* surface of bitumen-coated quartz slide. Finally, the film pressure for bitumen films spreading at the aqueous phase surface was measured as a function of pH with the Wilhelmy plate technique.

It was found that a balance of interfacial tensions in all these systems favors spreading of the bitumen at the gas bubble surface because of a positive spreading coefficient Filming occurs by the initial advancement of a thin film, "bitumen film precursor". This bitumen film precursor reduces the surface tension of the aqueous phase, and as a consequence, affects the driving force (spreading coefficient) for spreading. At room temperature, the gas bubble surface is covered by the bitumen film precursor during the first few seconds of contact between the phases. Subsequently, in a matter of minutes the bubble is enveloped by the bitumen film.

Although thermodynamic conditions favor envelopment of the gas bubble by bitumen, several discontinuities in the thickness of the thin films (bitumen film precursors) were observed with a microscope. For oil sand systems, fine mineral particles with hydrophobic properties further complicate the bitumen spreading over the gas bubble surface and promote the formation of bitumen islands.

INTRODUCTION

The physical properties, fractional composition and elemental analyses of bitumen from oil sand deposits differ from one deposit to another, and even between samples from the same deposit (see Ref.(l) for a recent review of the work on Utah oil sand characterization). Also, the mineralogical composition (including bitumen content), its consolidation and bitumen-mineral surface bonding may differ between oil sands from different sources. These differences between oil sands, sometimes very significant, reinforce the point that one processing strategy for bitumen separation may not be applicable to all oil sands. Although surface-mining or *in-situ* technology can be used for bitumen recovery from oil sand deposits (2), only surface-mining and processing technology has been used commercially for the Canadian deposits (3). Specifically the hot-water process (bitumen "extraction" with water) is commercially practiced by both the Suncor Inc. and Syncmde Ltd. plants in Canada. Also, it was demonstrated at the University of Utah that this process, after several modifications, is applicable for bitumen separation from Utah oil sands (4-6).

Two main separation steps *must be accomplished in oil sand processing* with water; bitumen release from mineral matter, and bitumen recovery from the oil sand slurry. The density of oil sand bitumens is close to the density of water (1). Further, bitumen droplets released from the coarse sands contain fine mineral particles, which contribute to the bitumen droplet mass (1,7). This indicates that bitumen separation from the aqueous phase after bitumen release from oil sand cannot be realized simply based on buoyancy considerations and bitumen droplets must contain an appropriate amount of gas (or light solvent) to make them less dense than the processing water, in order to initiate bitumen separation. In this regard, separation of bitumen from digested oil sand is aided by flotation in the hot-water process. During flotation, the bitumen-air attachment occurs if repulsive forces (electrostatic nature) between bitumen/water and air/water interfaces are not too high to prevent this mechanism, and if steric barriers at the bitumen/water interface are not significant. After bitumen droplet attachment to the gas bubble a balance of interfacial tensions in the system favors spreading of the bitumen around the gas bubble (8). The kinetics of attachment between bitumen droplets and bitumen-enveloped gas bubbles may be completely different than for the attachment to bitumen-free gas bubbles. Unfortunately, all these mechanisms, i.e., bitumen droplet-gas bubble attachment and bitumen spreading at the water surface, are poorly understood and further research effort in this area is needed. The mechanisms associated with bitumen separation from oil sands in the hot-water process have been analyzed at the University of Utah in recent years (1,7,9-11). It is believed that continued progress in understanding the surface chemistry fundamentals may stimulate further improvements in the bitumen separation technology. In this regard, additional discussion on the mechanisms of bitumen separation from oil sands in hot water processing is presented in this contribution. Bitumen spreading over a gas bubble surface is demonstrated and the thermodynamics of such systems are discussed based on surface and interfacial tension values.

EXPERIMENTAL

Reagents

The bitumen used in this study was that extracted with spectrograde toluene (Fisher Scientific) from oil sand samples mined from the northwest site of the Whiterocks deposit. The Whiterocks bitumen was reported to be composed of 29.2-30.2 wt% saturates, 16.8-24.8 wt% aromatics, 40.2-43,1 wt% resins and 3.3-4.1 wt% asphaltenes; with the molecular formula for this bitumen to be $C_{35}Hj_{g}Nl_{)}j,S_{(1.0\%}O_{(1)1}$ (12). The specific gravity of bitumen was determined to be 0.98-0.99 (15.6:15.6"C), and the viscosity was found to be 32-39 Pa s at 50°C (12).

The basic chemicals used in the experiments were distilled and deionized water; analytical grade sodium carbonate, sodium chloride, sodium hydroxide, and hydrochloric acid (Mallinckrodt Inc.); and spectrograde chloroform (EM Science). Kerosene (874 kg/m^3 density) was received from Chevron.

Microscopic Observations of Bitumen Spreading at the Gas Bubble Surface

Samples of the unconsolidated Whiterocks oil sand (from the northwest site; 7.6 wt% bitumen) treated with 10 *wt%* kerosene (addition based on the bitumen content) were submerged in alkaline solutions in a glass cell and the changes in sample characteristics, especially bitumen spreading at the gas bubble surface, were observed through a stereoscopic microscope (Carl Zeiss Jena, Germany) and photographs taken as appropriate. The temperature in the glass cell was maintained at a constant level (+3°C) by using a hot plate, and the pH of the aqueous phase was measured using a pH-meter (model 520, Orion Research Inc.).

The toluene-extracted Whiterocks bitumen with 10 wt% kerosene was spread mechanically on a quartz slide. The quartz slide was immersed in the aqueous phase and an air bubble, pushed through a microsyriitge, was attached to the bitumen coated surface of the quartz slide. Bitumen spreading over the air bubble was observed and photographed through the stereoscopic microscope.

Surface Tension Measurements

The surface tension was measured with a Digital-Tensiometer K10T (KRUSS, GmbH; Germany) using the Wilhelmy platinum plate. An absolute accuracy for this method was 0.2 mN/m. The tensiometer was calibrated using distdled/deionized and organic-free water with a surface tension of 72.8 mN/m at 21°C.

The surface tension of the aqueous phase (0.001 M NaCl with varying pH as adjusted with HC1 or NaOH) was measured with the tensiometer and recorded as the value for zero time. The platinum plate remained in contact with the aqueous phase and the tensiometer remained in the "run" option to record any changes in surface tension. Next, a glass slide with a 0.3-0.6 mm thick bitumen layer (Whiterocks bitumen with 10 wt% kerosene was spread mechanically on a glass slide to form this coating) was immersed into the aqueous phase and the surface tension value for the aqueous phase was recorded as a function of time. Figure 1 shows the schematic diagram of this experiment. Immediately after contact of bitumen with the aqueous phase, the bitumen or bitumen components migrated over the surface of the aqueous phase causing changes in the surface tension value recorded by the tensiometer. The difference between the surface tension for the bitumen-free aqueous phase and the surface tension for the bitumen-coated aqueous phase is reported as the film pressure (referred as the "bitumen fdm precursor pressure" in the next part of this paper).

In other experiments, 0.342 g of the Whiterocks bitumen with 10 wt% kerosene was dissolved in *100 mL chloroform. From this* solution *25* uL was spread ar the aqueous phase surface in the sample container of the tensiometer using a microsyringe. The solvent was evaporated at room temperature (21-22°C) for 10-15 min. As calculated, a bitumen fdm of about 54 mg/m' with a thickness of 30-35 urn was created in this way. The surface tensions for the aqueous phase and the aqueous phase covered with a bitumen film were measured using the Wilhelmy plate technique.

RESULTS AND DISCUSSION

Bitumen Spreading at the Gas Bubble Surface in Oil Sand Systems

Samples of the Whiterocks oil sand were submerged in alkaline solution in a glass cell and the changes in the oil sand sample were observed using the stereoscopic microscope. The observations mainly concentrated on the mechanism of bitumen migration from coarse mineral particles onto the gas bubble surface.

As reported in previous contributions (1,7), the contact of oil sand with alkaline water, particularly at elevated temperature, resulted in the identification of the following mechanisms; (a) bitumen film rupture and bitumen lens formation at coarse particle surfaces, (b) gas (probably air, saturated with volatile hydrocarbons) release from oil sand structure and gas bubble formation on the oil sand surface, (c) bitumen spreading over the gas bubble surface, (d) rupture of the bitumen bridges between sand grains, and (e) release of bitumen-enveloped gas bubbles and bitumen droplets. The extent

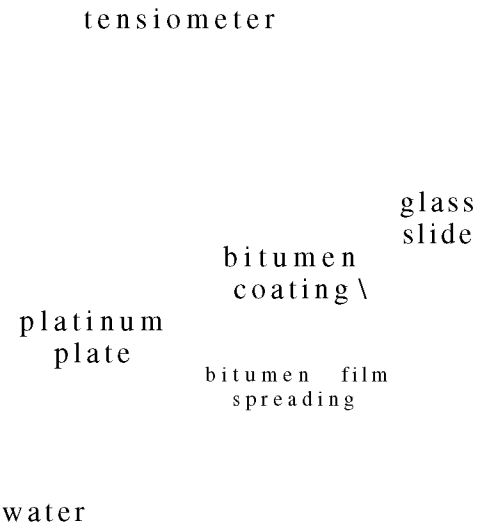

Figure 1. Illustration of the dynamic surface tension measurement for water in contact with bitumen.

to which each mechanism contributes to the release and separation of bitumen depends on the aqueous phase composition (pH and reagents concentration) and experimental conditions (temperature, reaction time, hydrodynamic conditions in the reaction cell, etc.). Photographs, which are presented in Figure 2, show a Whiterocks oil sand sample immersed in an alkaline solution, where photograph A was taken immediately after sample immersion, and photograph B taken 5 minutes after sample contact with the aqueous phase. It was found that gas bubbles carrying the bitumen (both thin bitumen film and bitumen "islands") cover the oil sand sample. The details of these systems can only be recognized from color photographs (unfortunately, black and white photographs could only be published in these proceedings). A few color photographs have already been presented in our previous contributions (1,9).

Among all of the mechanisms observed for oil sand samples submerged in an aqueous phase with varying pH (from pH 8.0 *to* pH 11.0) and varying ionic strength (0.001 M to 1 M NaCl, 0.00] M to 0.1 M Na_3PO_4), only the migration of bitumen from sand grains onto the gas bubble surface was of particular concern in this contribution. Thus, it was observed that the hydrophobic properties of bitumen inhibited water penetration into the free space of the oil sand sample, and thus, air remained in this space at the very beginning of the contact of the oil sand with the aqueous phase. Gas entrapped in the oil sand sample was displaced by penetration of the aqueous phase and the gas displacement was facilitated with increasing temperature, pH and electrolyte concentration. This phenomenon was a consequence of the increasing hydrophilic properties of the bitumen surface as caused by the presence of natural surfactants; components of the bitumen (see experimental results for the dynamic bitumen/water interfacial tension measurements presented in the previous contribution (1)). The increased activity of ionized carboxylic acids in alkaline solutions is well recognized (13). For example, the bitumen/water interfacial tension decreases with an increase in both pH and ionic strength of the aqueous phase (1,7).

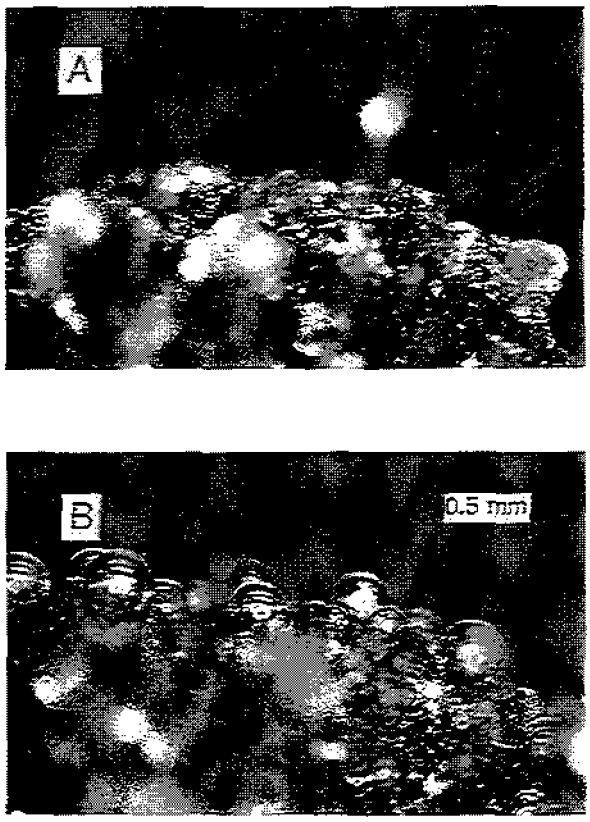

Figure 2. The structure of the Whiterocks oil sand sample submerged in alkaline solution (pH 9.0, T=50°C) after 15 seconds (A), and after 5 minutes (B).

Gas displaced by the aqueous phase from the oil sand sample, formed small bubbles around the oil sand sample (see photograph B in Figure 2), which adhered to coarse mineral particles via bitumen bridges. The bitumen spread over the gas bubble surface to envelope the bubble, mostly as a thin fdm (referred to as the "bitumen fdm precursor" in the next part of this paper) but sometimes as a thick envelope (referred to as the "bitumen film" in the next part of this paper) if a small bubble was attached to a locally bitumen-rich oil sand spot, or to form an "island" of bitumen surrounded by a bitumen film precursor. Often, the bitumen was already picked-up by the gas bubble from the pore space of the oil sand sample during gas migration to the outer zone of the sample, and thus, some gas bubbles migrated through the oil sand sample to the surface carrying a bitumen film/island.

Bitumen islands containing fine particles were frequently formed at the gas bubbles' surfaces instead of uniform film formation (a schematic of such a system is presented in Figure 3). However, the bitumen film precursor was always observed to surround the entire gas bubble surface for these systems. These bitumen film precursors could be distinguished due to the rainbow of colors evident from reflected light. The fine particles with hydrophobic properties hindered the spreading of bitumen (thus forming an island) over the gas bubble surface according to capillary forces. The hydrophobicity of these fine particles is concluded from the observation that these mineral particles were immersed much deeper into the bituminous phase than into the aqueous phase (at moderate pH). Increasing alkalinity of the aqueous phase increased the exposure of the particles to the aqueous phase. X-ray diffraction analysis

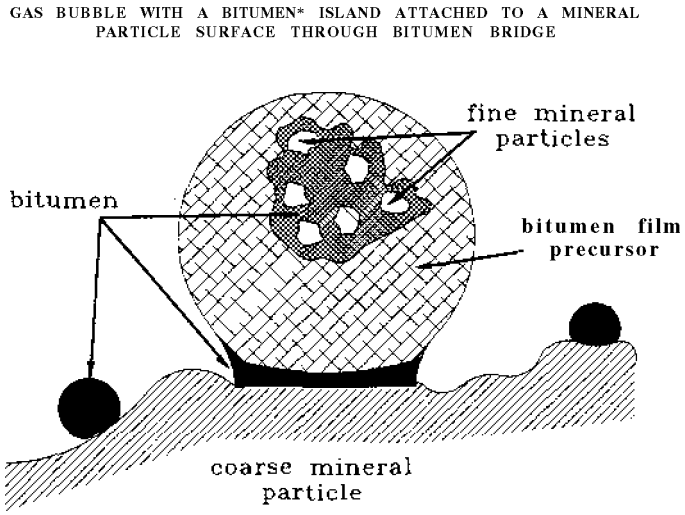

Figure 3. The nature of gas bubbles observed through a microscope for oil sand samples in alkaline solutions.

of the mineral matter distribution during the hot water processing of the Whiterocks oil sands showed that mostly fine calcite and dolomite particles tend to accumulate in the bitumen concentrate, however, quartz and kaolinite particles were also present in the bituminous froth (1).

Bitumen Spreading at the Air Bubble Surface in Model Systems

Bitumen spreading at the air bubble surface was also observed in the following model systems. A quartz slide was coated with bitumen (10 wt% kerosene) and submerged into the aqueous phase of varying pH (from pH 2 to pH 11) and electrolyte concentration (0-0.05 M $Na_2P_4O_{10}$; 0-1 M Nad). An air bubble was attached to the bitumen-coated slide using a microsyringe and the spreading of the bituminous phase over the bubble surface was observed through the stereoscopic microscope. A photographic record of the events was made. Figures 4 and 5 illustrate the kinetics of the bitumen spreading (the color photographs of bitumen spreading for similar model systems have been presented previously (1,9)).

It was observed that the bituminous phase always tended to cover the entire surface of the air bubble for a variety of aqueous phase compositions: pH 2-11; 0-0.05 M Na^O^ or 0-1 M NaCl concentrations; and temperature from 20 to 60°C (only a few observations of bitumen spreading at the gas bubble surface were carried out at elevated temperature, and additional experiments are in progress). Microscopic observations showed that bitumen spreading involves complex phenomena and that the mechanisms of bitumen spreading in these model systems are similar to those observed for oil sand samples (see previous section). For example, it was found that the bitumen fdm precursor always assisted the moving bitumen film and this bitumen film precursor covered the bubble surface during the first seconds of the experiment. Although our experimental approach did not allow us to record the existence and kinetics for the spreading of this film precursor in any quantitative way, a change in color of the air bubble surface in front of the thick bitumen film, moving slowly as a "bulk" phase was quite clear. Only the front of this bitumen film can be distinguished from the black and white photographs *shown* in Figures 4 and 5. The bitumen film precursor can not be *seen in* these black and while photographs.

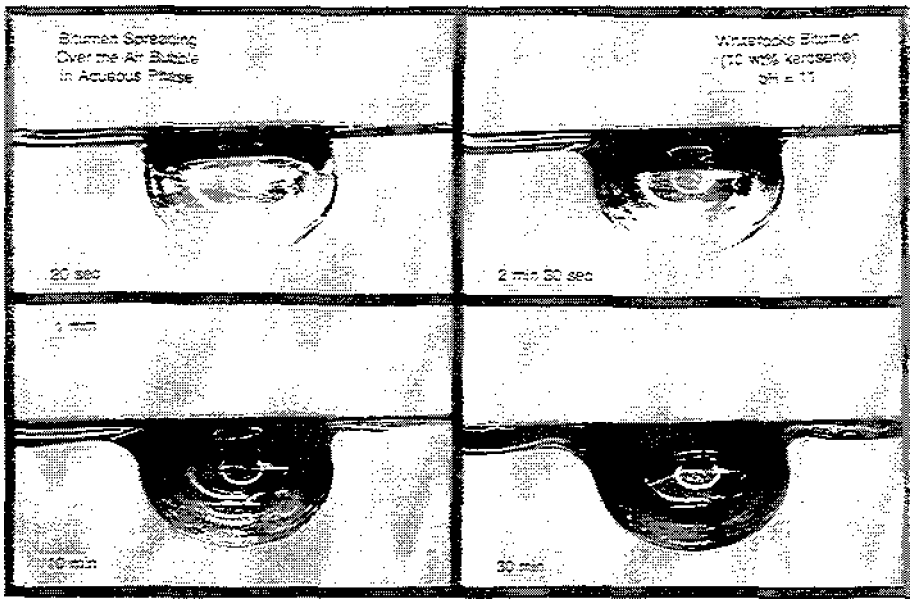

Figure 4. Kinetics of spreading of the Whiterocks bitumen (diluted with 10 wt% kerosene) at the air bubble surface; pH 11, T=21°C.

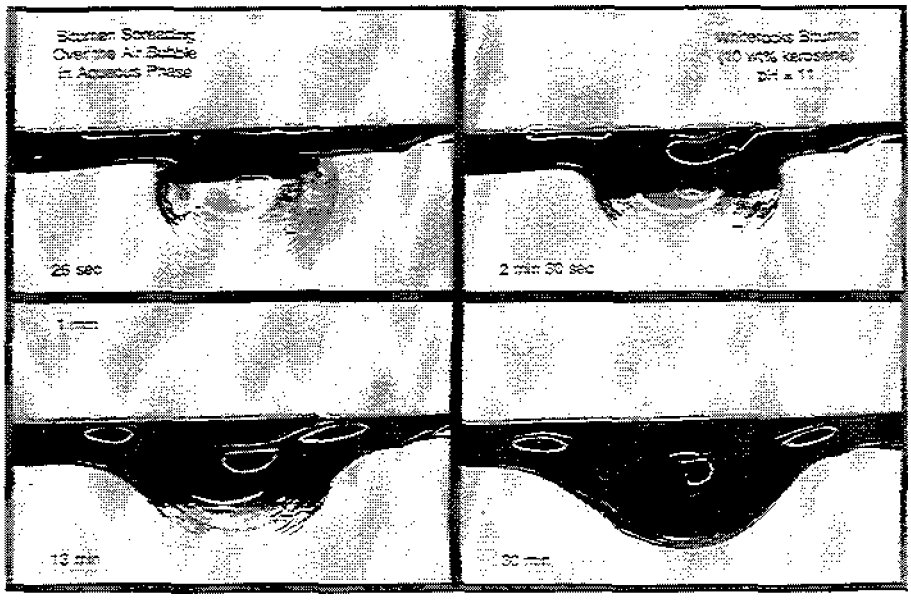

Figure 5. Kinetics of spreading of the Whiterocks bitumen (diluted with 10 wt% kerosene) at the air bubble surface; pH 11, T=21°C. The bitumen is in excess of the amount used in the experiment presented in Figure 4.

It appears that different mechanisms govern the spreading of the bitumen film precursor and the bitumen film. The bitumen film spreads very slowly compared to the bitumen film precursor. It was found that only a decrease in the temperature of the aqueous phase had a detrimental effect on the spreading kinetics of the bitumen film. Spreading of the bitumen film was not influenced by the aqueous phase composition. This suggests that the spreading velocity of the bitumen film depends mainly on the physical properties of bitumen such as viscosity and density. Further experiments leading to a quantitative description for the kinetics of bitumeu spreading are now in progress at our laboratory.

Although the kinetics of spreading for the bitumen film can be described quite clearly to be *independent of the* aqueous phase composition, spreading of the bitumen film precursor was *too fast to* make any rationale conclusion on the mechanism associated with the spreading kinetics. Also, no conclusion could be drawn regarding the thickness of the bitumen film precursor for different aqueous phase compositions (pH and electrolyte concentration). The experimental data on bitumen film precursor pressure, which are presented in the next section, provide useful insights into the nature of the formation of such thin bitumen films at the water surface.

Finally, although bitumen appeared to spread freely over the water surface increased microscopic magnification of the bitumen film precursors showed several discontinuities in their thickness (Figure 6). "Holes" in file thin fUrn (bicumen film precursor) were frequently observed for several systems, even after equilibration of the system for several hours. The origin of these discontinuities is not known at this time. It seems that thin films of a certain thickness are thermodynamically unstable. These "holes" were not covered by the next layer of spreading bitumen. However, such "holes" were not always observed, particularly when the bitumen was in significant excess and could form a thick layer around the *gas* bubble (encapsulation of the *gas* bubble in the bitumen mass). In such cases, the force of gravity for the spreading bitumen was large enough to overcome the energy barriers associated with the "holes". The "holes" found in the bitumen film precursors may be sirniiar to Newton black films observed in foams (14). If this is the case, the isotherm for the disjoining pressure should demonstrate two minima responsible for the stability of bitumen films of varying thickness (note that the disjoining pressure is the difference between the pressure operating in the bitumen film, between r^rnmen/air and bitumen/water interfaces, and the pressure in the bulk bitumen with which the film is connected and is in equilibrium). Bitumen film precursors with a thickness which is between these two minima will be unstable. Unfortunately, no experimental work has been done to examine the disjoining pressure isotherms for thin bitumen films.

Figure 6. Discontinuities in bitumen film precursor surrounding the air bubble in an aqueous phase; 0.001 M NaQ, pH 6, T=2I°C. It should be noted that these discontinuities, "holes", really represent a region of the film of smaller thickness.

Bitumen Film Precursor Pressure

The dynamic surface tension measurements for water with varying pH in *contact* with the Whiterocks bitumen (diluted with 10 wt% kerosene) were carried out with the Wilhelmy plate technique (see Experimental section and Figure 1 for details). It was observed during the surface tension measurements that spreading of the bitumen always resulted in a uniform thin film over the entire surface of the aqueous phase, and no significant variation of the thin film thickness (according to color of the reflected light) was observed at the aqueous phase surface when the pH was changed. The experimental results are shown in Figure 7 as a correlation between bitumen film precursor pressure and time. The bitumen film precursor pressure is the difference between the surface tension of the aqueous phase used in these experiments (typically between 72.0 and 72.8 mN/m) and the surface tension of this phase covered with a bitumen film precursor (the bitumen film migrated from a glass slide which we believe is similar to the bitumen film precursor observed in bitumen spreading over gas bubbles at the oil sand sample surface; see previous sections).

As shown in Figure 7, the bitumen film precursor pressure was strongly affected by the pH of aqueous phase. The largest effect of the bitumen film precursor on the surface tension of the aqueous phase was observed for both strongly alkaline solutions and strongly acidic solutions (see also Figure 8 which shows the correlation between the bitumen film precursor pressure and the pH of water after 20 minutes of equilibration). This dependence is in an agreement with the relationship between the bitumen/water interfacial tension and aqueous phase pH, which was reported in our previous contributions (1,7).

Unfortunately, based on the results presented herein, no conclusions could be drawn regarding the kinetics of bitumen fdm precursor spreading at the aqueous phase surface. The bitumen film precursor pressure changed faster during bitumen spreading over the alkaline and acidic solutions when compared to the results at moderate values of pH (see Figure 7), and it can be attributed to the kinetics of bitumen spreading as well as to diffusion of molecules, their rearrangements, dissociation of surface-active species at the bitumen/water interface, etc. For example, different film pressures were recorded for varying pH even for the same amount of bitumen which covered the water surface (see Figure 9).

Thermodynamics of Bitumen Spreading at the Water Surface

Bitumen spreading at the water surface requires a positive spreading coefficient (S>0), where the spreading coefficient is expressed by the following equation (15):

$$\$ \; IV - (taw \cdot \Phi \qquad (1)$$

with y_w, y_B, y_{BW} as the interfacial tension for water, bitumen, and bitumen/water, respectively.
In detailed analysis of the oil sand systems with dispersed phases (oil sand slurry) changes in the interfacial areas and electrical contributions to the free energy of the system should also be considered (S).

It was demonstrated in our previous contributions (1,7) that the spreading coefficient as calculated based on equilibrium values of y, y_B, and y_{BW}, should remain positive for the Whiterocks bitumen/water systems with varying pH (from pH 7 to pH 11) and for varying electrolyte concentration (0-0.05 M $Na_4P_2O_7$; 0-1 M NaCl), even if the surface tension of the processing water is reduced to 45 mN/m. Ji is shown in this contribution that the bitumen film precursor may reduce the surface tension of the aqueous phase to values of less than 45 mN/m. For example, the surface tension of water at pH 11 was reduced by the bitumen film precursor to a value of about 37 mN/m (see Figure 8). A longer time of equilibration than that used in this study (t>20 min) as well as replacement of the model aqueous phase with processing water from hot-water process experiments may lead to even smaller film pressure values.

The surface tension of Whiterocks bitumen and the bitumen/water interfacial tensions were reported in the literature (1,7). For example, the surface tension of bitumen (diluted with 10 wt% kerosene) was found to be about 27 mN/m at 21°C. The interfacial tension between bitumen (10 wt%

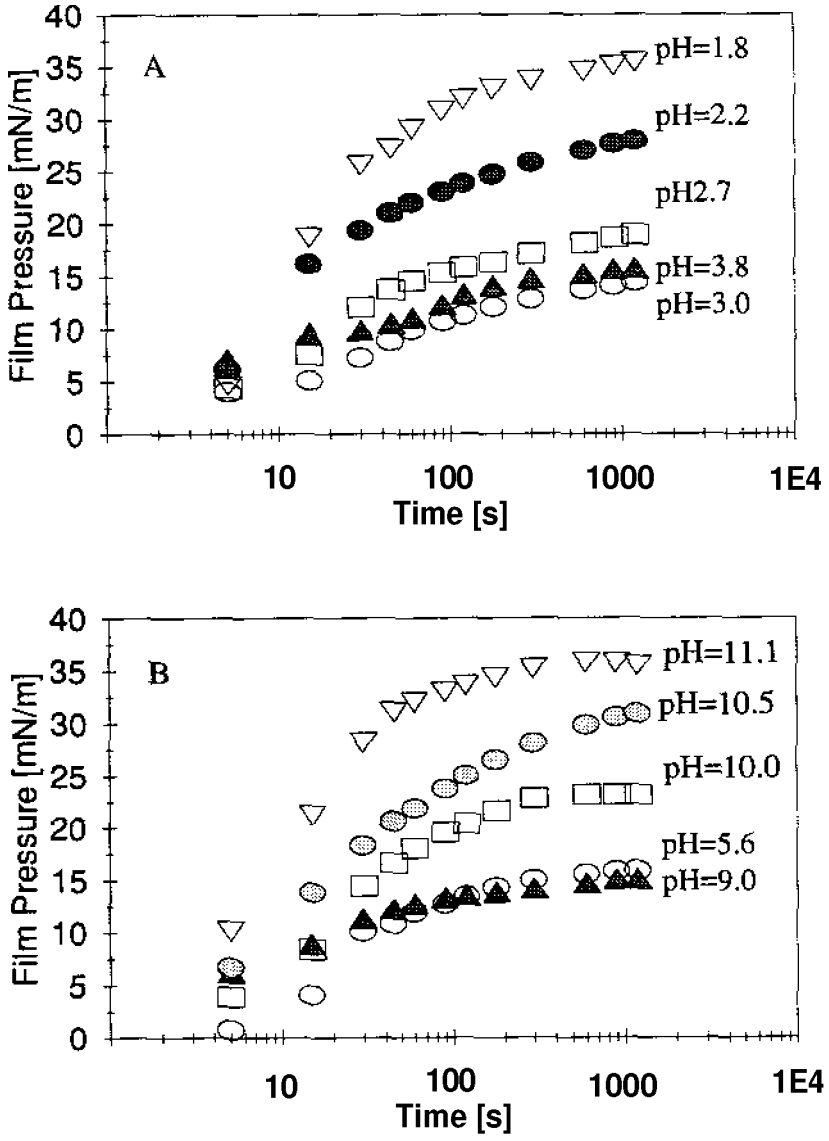

Figure 7. The dynamic bitumen film precursor pressure for the Whiterocks bitumen (diluted with 10 wt% kerosene) at aqueous phase surfaces (0.001 M NaCl) of varying pH, The measurements were carried out at a temperature of 21°C *using the* Wilhelmy plate technique.

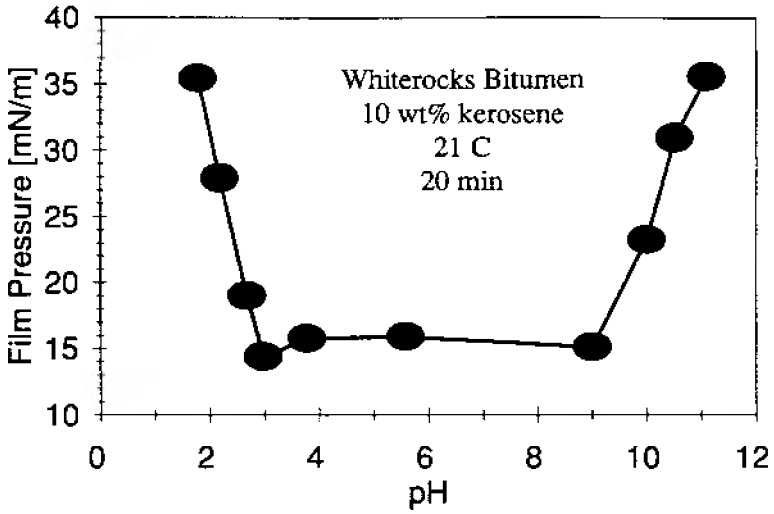

Figure 8. The effect of aqueous phase pH on bitumen film precursor pressure for the Whiterocks bitumen (diluted with 10 *wi%* kerosene) which had spread spontaneously over the aqueous phase surface (0.001 M NaCl). The measurements were carried out at a temperature of 21°C using the Wilhelmy plate technique. The phases, bituminous and aqueous phases, were equilibrated for 20 minutes.

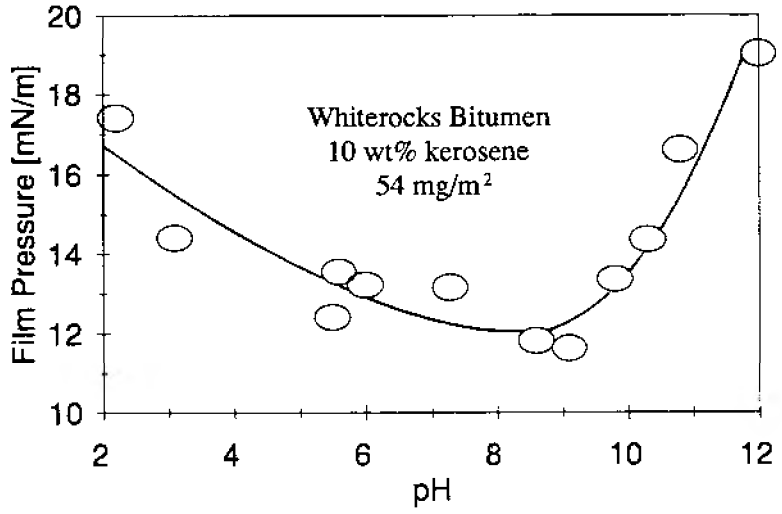

Figure 9. The bitumen film pressure for the Whiterocks bitumen film (10 wt% kerosene) with a thickness of about 30-35 pm (54 mg/m^2) as a function of pH, as measured with the Wilhelmy plate technique. It was observed in these measurements that the bitumen film, formed by evaporation of solvent, was not perfectly distributed over the aqueous phase surface (0.001 M NaCl) and demonstrated a slight variation in thickness.

kerosene) and water depends on pH and was found to be about 18-20 mN/m for pH 6-9 and a temperature of 60"C. This value drops to near zero for either strongly acidic solutions (pH 2) or strongly alkaline solutions (pH 11), at 60°C (1,7). The temperature coefficient of the interfacial tension in such systems was also found to be dependent on pH (1). Recorded values for the temperature coefficient of the interfacial tension between Whiterocks bitumen and the aqueous phase are from -(0.03-0.05) mN/(m deg) at pH 3-8 to near zero at pH 9-10 (1,7). If all these literature data on surface/interfacial tension for Whiterocks bitumen and the experimental data for bitumen film precursor pressure presented in this contribution (see Figure 8) are accomodated into Equation (I) it appers that the spreading coefficient approaches a near zero value (roughly 5-12 mN/m) when the air/bitumen/water system equilibrates. Unfortunately, the exact value for the spreading coefficient is difficult to determine in such dynamic systems. A 1-3 mN/m scatter in the value of each surface and interfacial tension was frequently observed during the *measurements because* of variation in equilibration time, varying residual solvent content in bitumen samples, light hydrocarbon fraction evaporation, pH instability, etc. In this regard, the siirface/interfacial tension data remain uncertain at a level of 1-3 mN/m accuracy, and consequently, our rough estimate of the spreading coefficient remains uncertain at a level of 3-9 mN/m. However, even with such error it is clear that the spreading coefficient should be very small at the end of mutual saturation between the phases.

The bitumen spreading at the water surface is a dynamic process in which the driving force, the spreading coefficient, may vary with time. It was shown that the spreading coefficient can change even for systems with pure single-component liquids and that the initial positive spreading coefficient decreases to near zero or becomes negative when liquids are saturated with each other (15,16). Bitumen is a complex mixture of hydrocarbons. The equilibration of the surface properties in the bitumen/water systems requires time, and the spreading phenomena are even more complex than for pure systems. Microscopic observations, discussed in the previous sections, showed that the bitumen film precursor always assists in the spreading of bitumen and reduces significantly the surface tension of aqueous phase. The surface tension of the aqueous phase in contact with bitumen decreases with time due to a screening effect which is created by the migrating bitumen, or selected bitumen components. Further, contact of bitumen with the aqueous phase also creates diffusional processes in which surface-active compounds migrate at the bitumen/water interface to minimize the interfacial free energy (1), In this regard, the spreading coefficient for the bitumen/water system varies with time due to changes in the surface tension of the aqueous phase, affected by the spreading films of bitumen (or bitumen components), and changes of the bitumen/water interfacial tension. Bitumen spreading at the water surface occurs as long as the thermodynamic equilibrium in the system is not reached, i.e., there is a positive spreading coefficient.

CONCLUSIONS

After Whiterocks bitumen (10 wt% kerosene) droplet attachment to a gas bubble a balance of interfacial tensions in the system favors spreading of the bitumen over the entire gas bubble rather than formation of bitumen lenses. The bitumen spreads over the air bubble surface because of a positive spreading coefficient. It seems that the spreading coefficient reaches a near zero value when the system approaches the equilibrium state.

The initial spreading of a bitumen film precursor always assists the spreading bitumen film. *The* bitumen film precursor covers the bubble surface spontaneously during the first seconds of bitumen contact with a gas bubble. This film reduces the surface tension of the aqueous phase significantly. The bitumen film precursor pressure depends on the pH of the aqueous phase and increases for both alkaline and acidic solutions. The driving force for the spreading of the bitumen film precursor may originate from diffusional processes after molecular interactions.

The bitumen film follows the bitumen film precursor, but very slowly. According to microscopic observations it appears that the kinetics of spreading depends on the physical properties of bitumen; viscosity and density. The Whiterocks bitumen is able to envelope the air bubble for a wide variety of aqueous phase compositions: various values of pH and electrolyte concentration.

For the first time, it is demonstrated that although thermodynamic conditions favor the bitumen

spreading over the gas bubble surface, discontinuities in bitumen film thickness appear for certain conditions. The origin of these "holes", particularly observed for the bitumen film precursors, remains unknown.

In real oil sand systems, fine hydrophobic particles further complicate the bitumen spreading over the gas bubble surface. It was observed for the Whiterocks oil sands submerged in alkaline solutions (varying pH and electrolyte concentration) that fine mineral particles remained in the bituminous phase during its spreading at the gas bubble surface and they forced the formation of bitumen islands at the bubble surface instead of the formation of a film of uniform thickness.

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